PALLADIUM-CATALYZED [3+2] ANNULATION OF meso-BROMOPORPHYRINS WITH SILYLACETYLENES AND DESILYLATION OF 8a-SILYL-7,8-DEHYDROPURPURIN

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Abstract – Palladium-catalyzed [3+2] annulation of meso-bromoporphyrins with trimethylsilyl-, tert-butyldimethylsilyl-, and triisopropylsilylacetylenes afforded 8a-silyl-7,8-dehydropurpurins. Protodesilylation of 8a-trimethylsilyl-7,8-dehydropurpurin resulted in the first synthesis of an 8a,8b-unsubstituted 7,8-dehydropurpurin.

INTRODUCTION

The electronic nature of a porphyrin ring is susceptible to modifications through fusion of π-conjugated segments at the periphery. Chemists have hence devoted much time to the design and synthesis of novel π-extended fused porphyrins.1,2 Among them, 7,8-dehydropurpurins are intriguing porphyrinoids that bear a fused five-membered ring that includes a vinylene moiety bridging across the meso and β positions.3–7 They exhibit largely altered absorption reaching out to the near infrared region due to their forbidden HOMO–LUMO transition with a narrow energy gap. These properties arise from the presence of dual 18π- and 20π-electronic circuits that resonate in the conjugated macrocycles.3 Today, a variety of 7,8-dehydropurpurin derivatives have been synthesized, which contain various substituents like aryl,4 alkynyl,5 and porphyrinyl1,5,6 groups at their 8a- and 8b-positions. In addition, fused π-segments such as phenylene7 and thienylene3 also behave as bridging vinylene moieties. However, 8a,8b-unsubstituted 7,8-

This paper is dedicated to Professor Isao Kuwajima on the occasion of his 77th birthday.
dehydropurpurin has been unexplored. Our continuing interest in porphyrin \( \pi \)-systems encouraged us to envisage synthesizing a 7,8-dehydropurpurin having no substituent at the bridging vinylene moiety. Investigation into the \( \text{8}^a,\text{8}^b \)-unsubstituted 7,8-dehydropurpurin should be helpful to elucidate the intrinsic nature of its attractive \( \pi \)-system.

Recently, we reported the facile synthesis of 7,8-dehydropurpurin derivatives via Pd-catalyzed \([3+2]\) annulation of meso-bromoporphyrin with diphenylacetylene.\(^4\)\(^8\) According to this procedure, we have synthesized \( \text{8}^a \)-silyl-7,8-dehydropurpurins by replacement of diphenylacetylene with terminal trimethylsilyl- (TMS-), tert-butyldimethylsilyl- (TBS-), and triisopropylsilyl- (TIPS-) acetylenes. Desilylation reaction of \( \text{8}^a \)-TMS-7,8-dehydropurpurin led to the first synthesis of an \( \text{8}^a,\text{8}^b \)-unsubstituted 7,8-dehydropurpurin.

**RESULTS AND DISCUSSION**

Initially, we performed Pd-catalyzed \([3+2]\) annulation of Ni\(^{11}\) meso-bromoporphyrin \( \text{1Ni} \) with TMS-, TBS-, and TIPS-acetylenes in the presence of catalytic amount of Pd\(_2\)(dba)_3 and PPh\(_3\) (Scheme 1). The reaction of \( \text{1Ni} \) with TMS-acetylene afforded the expected \( \text{8}^a \)-TMS-7,8-dehydropurpurin \( \text{3a} \) in low yield (29%) with some side products. In the case of a bulkier TBS group, Sonogashira coupling\(^9\) competed with the desired \([3+2]\) annulation to provide TBS-ethynylporphyrin \( \text{2b} \) and \( \text{8}^a \)-TBS-7,8-dehydropurpurin \( \text{3b} \) in 23% and 41% yields, respectively. Such competitive Sonogashira coupling has been reported in the Pd-catalyzed \([3+2]\) annulation reactions of 9-bromoanthracene with terminal acetylenes.\(^10\) The steric hinderance caused by the bulkiest TIPS group prevented the desired \([3+2]\) annulation to afford a small amount of \( \text{8}^a \)-TIPS-7,8-dehydropurpurin \( \text{3c} \) (9%) and a good yield of TIPS-ethynylporphyrin \( \text{2c} \) (66%).

![Scheme 1. Pd-Catalyzed [3+2] annulation of 1Ni with silylacetylenes. Ar = 3,5-di-tert-butylphenyl](image)

After extensive screening of porphyrin substrates and reaction conditions, we found that utilization of free base meso-bromoporphyrin \( \text{1H}_2 \) as a starting material and \((\text{o-tol})_3\)P as a ligand is more effective for annulation (Scheme 2). The Pd-catalyzed \([3+2]\) annulation of \( \text{1H}_2 \) with TMS-acetylene followed by...
nickel metalation furnished 3a in 52% yield as a sole isomer without any alkynylporphyrins. By considering the previously reported reaction of 9-bromoanthracene with TMS-acetylene,\textsuperscript{10,11} the carbopalladation of porphyrinylpalladium to the C–C triple bond occurred to minimize steric hinderance, providing the 8\textsuperscript{a}-silylated compound selectively. Even in the cases of bulkier silyl groups like TBS and TIPS groups, the [3+2] annulation reactions also proceeded smoothly and gave 3b and 3c in 75% and 66% yields, respectively.

![Scheme 2](image)

**Scheme 2.** Pd-Catalyzed [3+2] annulation of 1H\textsubscript{2} with silylacetylenes. Ar = 3,5-di-\textit{tert}-butylphenyl

Protodesilylation of 3a with hydrochloric acid in aqueous THF afforded unsubstituted 7,8-dehydropurpurin 4 in 45% yield (Scheme 3). The \textsuperscript{1}H NMR spectrum of 4 in CDCl\textsubscript{3} showed two upfield-shifted doublet signals owing to the two protons at the bridging vinylene moiety at 6.80 and 5.96 ppm \((J = 5.5 \text{ Hz})\). In the case of pyracylene, which had dual 10\texttextsuperscript{\pi}- and 12\texttextsuperscript{\pi}- electronic circuits, the paramagnetic ring current also resulted in relatively high field-shifted signals at 6.01 and 6.52 ppm in CCl\textsubscript{4}.\textsuperscript{12} The \textsuperscript{13}C–\textsuperscript{1}H COSY measurement revealed the \textsuperscript{13}C signals of the fused five-membered ring at 139.35 and 126.18 ppm (Supporting Information, Figure S13). Unfortunately, compared with the previously reported 8\textsuperscript{a},8\textsuperscript{\alpha}-substituted 7,8-dehydropurpurin derivatives,\textsuperscript{3–7} 4 was less stable in solution and gradually decomposed to a complicated mixture. Probably, the substituents at the fused five-membered
rings kinetically suppressed their oxidative decomposition processes despite its inherent instability caused by the contribution of 20π-antiaromatic conjugations.

The UV-visible absorption spectra of 3a–c, 4, and 8a,8b-diphenyl-7,8-dehydropurpurin 54,6 in CH2Cl2 are shown in Figure 1. These absorption spectra have characteristic split Soret bands located at 350–500 nm, almost featureless Q-like bands around 580 nm, and weak and extremely broad bands almost reaching 1000 nm. The absorption spectra of 3a–c and 4 are almost similar because of the exiguous perturbations of the silyl groups to 7,8-dehydropurpurin π-systems. Compared with 5, 4 has slightly blue-shifted absorption bands in the overall region. Although the phenyl groups at the 8a- and 8b- positions of 5 were twisted out of the porphyrin plane,4,6 they could contribute to the π-extension of the 7,8-dehydropurpurin π-system to a small degree.

Figure 1. UV-Visible absorption spectra of (a) 3a–c and (b) 4 and 5 in CH2Cl2

![Figure 1](image)

Table 1. Redox potentials of 2a–c, 4 and 5[a]

<table>
<thead>
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<th>oxidation (V)</th>
<th>reduction (V)</th>
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<th>E1/2red</th>
<th>E1/2ox</th>
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<td>3a</td>
<td>0.24</td>
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<td>−2.04</td>
<td>*0.74</td>
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<tr>
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<td>−1.51</td>
<td>*0.75</td>
<td>−2.04</td>
<td>*0.74</td>
<td>−1.90</td>
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<tr>
<td>3c</td>
<td>0.24</td>
<td>−1.53</td>
<td>*0.74</td>
<td>−2.04</td>
<td>*0.74</td>
<td>−1.90</td>
</tr>
<tr>
<td>4</td>
<td>0.24[b]</td>
<td>−1.51</td>
<td>—</td>
<td>−2.04</td>
<td>—</td>
<td>−1.90</td>
</tr>
<tr>
<td>5</td>
<td>0.19</td>
<td>−1.47</td>
<td>*0.64</td>
<td>−2.04</td>
<td>*0.64</td>
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</table>

[a] The redox potentials were measured by cyclic voltammetry in anhydrous CH2Cl2 with 0.1 M Bu4NPF6 as a supporting electrolyte, and Ag/AgClO4 as a reference electrode. Ferrocene/ferrocenium ion couple was used as an external reference. [b] Irreversible peak.
The electrochemical properties of 3a–c, 4 and 5 were studied by cyclic voltammetry (CV) in CH₂Cl₂ (Table 1). 8a-Silyl-7,8-dehydropurpurins 3a–c exhibited two reversible oxidation waves and one reversible reduction wave. Unsubstituted 7,8-dehydropurpurin 4 displayed a similar reversible reduction wave, but its first oxidation wave became irreversible. Lack of kinetically protecting groups at fused five-membered ring destabilized the radical cation and triggered off the decomposition of 4. Compared with 3a–c and 4, 5 exhibited a slightly smaller electrochemical HOMO–LUMO gap because of the contribution of phenyl groups to the π-extension.

In conclusion, Pd-catalyzed [3+2] annulation of free base meso-bromoporphyrin 1H₂ with three terminal silylacetylenes furnished 8a-silyl-7,8-dehydropurpurins 3a–c. Protodesilylation of 3a with hydrochloric acid resulted in the first synthesis of an unsubstituted 7,8-dehydropurpurin 4. By comparing the characters of unsubstituted 4 and substituted 5, the substituents at the fused five-membered rings of previously reported 7,8-dehydropurpurin derivatives have some contribution to their stability and π-extension.

**EXPERIMENTAL**

1H NMR (600 MHz), 13C NMR (151 MHz), and 13C–1H COSY spectra were taken on a JEOL ECA-600 spectrometer. Chemical shifts are reported on a delta scale in ppm relative to residual CHCl₃ (δ = 7.26 ppm) for 1H NMR and to CDCl₃ (δ = 77.16 ppm) for 13C NMR. Spectroscopic grade solvents were used for all spectroscopic studies without further purification. UV-visible absorption spectra were recorded on a Shimadzu UV-3600PC spectrometer. APCI-TOF-MS spectra were recorded on a Bruker microOTOF instrument using a negative-ion mode. Redox potentials were measured by cyclic voltammetry on an ALS electrochemical analyzer model 660. Preparative separations were performed by silica gel chromatography (Wako gel C-200, C-300, or C-400). Toluene was distilled from CaH₂. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

**Pd-Catalyzed [3+2] Annulation of Niᴵᴵ meso-Bromoporphyrins with Silylacetylenes:** The reaction of Niᴵᴵ meso-bromoporphyrin 1Ni with TBS-acetylene is representative: Niᴵᴵ meso-bromoporphyrin 1Ni (30 μmol, 30 mg), Pd₂dba₃ (3.0 μmol, 2.8 mg), and PPh₃ (12 μmol, 3.2 mg) were placed in a reaction flask under argon. Toluene (1.5 mL), TBS-acetylene (0.15 mmol, 28 μL), and N,N-dicyclohexylmethylamine (0.15 mmol, 32 μL) were added, and the whole mixture was heated at 110 °C for 12 h. The resulting mixture was allowed to cool to ambient temperature, diluted with CH₂Cl₂, and filtered through a small plug of silica gel with copious washings (CH₂Cl₂). After removal of the solvent in vacuo, the residue was purified by silica gel chromatography eluting with CH₂Cl₂/hexane. Recrystallization of the each separated solids from CH₂Cl₂/MeCN gave 2b (6.9 μmol, 7.4 mg, 23%) and 3b (12 μmol, 12.9 mg, 41%), respectively.
**2b:** $^1$H NMR (600 MHz, CDCl$_3$) $\delta = 9.52$ (d, 2H, $J = 5.0$ Hz, $\beta$), 8.83 (d, 2H, $J = 5.0$ Hz, $\beta$), 8.76–8.72 (m, 4H, $\beta$), 7.85 (d, 4H, $J = 1.9$ Hz, Ar-$o$), 7.84 (d, 2H, $J = 1.9$ Hz, Ar-$o$), 7.73 (t, 2H, $J = 1.9$ Hz, Ar-$p$), 7.71 (t, 1H, $J = 1.9$ Hz, Ar-$p$), 1.49 (s, 36H, tert-butyl), 1.46 (s, 18H, tert-butyl), 1.25 (s, 9H, TBS), 0.48 (s, 6H, TBS); $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta = 149.14$, 149.09, 145.21, 143.49, 142.82, 142.75, 139.96, 139.87, 133.37, 132.66, 132.30, 131.43, 128.80, 128.70, 121.90, 121.36, 121.31, 121.10, 106.28, 100.34, 98.51, 35.14 (overlap), 31.84, 31.81, 26.67, 17.39, –4.09 ppm; UV-vis (CH$_2$Cl$_2$): $\lambda_{\text{max}} (\varepsilon [\text{M}^{-1}\text{cm}^{-1}]) = 426$ (250000), 540 (17000), 573 nm (9600); MS (APCI, negative): $m/z = 1068.5941$. Calcd for C$_{70}$H$_{86}$N$_4$Si$_5$: 1068.5981 [M$^-$].

**2c:** $^1$H NMR (600 MHz, CDCl$_3$) $\delta = 9.55$ (d, 2H, $J = 4.6$ Hz, $\beta$), 8.82 (d, 2H, $J = 4.6$ Hz, $\beta$), 8.75–8.71 (m, 4H, $\beta$), 7.86–7.83 (m, 6H, Ar-$o$), 7.72 (d, 2H, $J = 1.9$ Hz, Ar-$p$), 7.70 (t, 1H, $J = 1.9$ Hz, Ar-$p$), 1.48 (s, 36H, tert-butyl), 1.46 (s, 18H, tert-butyl), 1.40–1.36 (m, 21H, TIPS); $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta = 149.12$, 149.08, 145.31, 143.48, 142.87, 142.77, 140.01, 139.92, 133.39, 132.64, 132.27, 131.45, 128.71 (overlap), 121.87, 121.37, 121.30, 121.08, 107.51, 98.88, 98.55, 35.15 (overlap), 31.85, 31.82, 19.21, 11.96 ppm; UV-vis (CH$_2$Cl$_2$): $\lambda_{\text{max}} (\varepsilon [\text{M}^{-1}\text{cm}^{-1}]) = 427$ (270000), 541 (17000), 573 nm (9800); MS (APCI, negative): $m/z = 1110.6415$. Calcd for C$_{73}$H$_{92}$N$_4$Si$_5$: 1110.6450 [M$^-$].

**Pd-Catalyzed [3+2] Annulation of Free Base meso-Bromoporphyrins with Silylacetylenes:** The reaction of free base meso-bromoporphyrin 1H$_2$ with TMS-acetylene is representative: Free base meso-bromoporphyrin 1H$_2$ (30 μmol, 28.6 mg), Pd$_2$(dba)$_3$ (3.0 μmol, 2.8 mg), and (o-tol)$_3$P (12 μmol, 3.7 mg) were placed in a reaction flask under argon. Toluene (1.5 mL), TMS-acetylene (0.15 mmol, 21 μL), and N,N-dicyclohexylmethylamine (0.15 mmol, 32 μL) were added, and the whole mixture was heated at 110 °C for 12 h. The resulting mixture was allowed to cool to ambient temperature, diluted with CH$_2$Cl$_2$, and filtered through a small plug of silica gel with copious washings (CH$_2$Cl$_2$). After removal of the solvent in vacuo, the residue was dissolved in toluene (10 mL). After addition of Ni(acac)$_2$·2H$_2$O (60 μmol, 15.4 mg), the mixture was stirred for 2 h at 110 °C. After removal of the solvent in vacuo, the residue was purified by silica gel chromatography eluting with CH$_2$Cl$_2$/hexane. Recrystallization of the separated solids from CH$_2$Cl$_2$/MeCN gave 3a (15.5 μmol, 15.9 mg, 52%) of high purity.

**3a:** $^1$H NMR (600 MHz, CDCl$_3$) $\delta = 8.35$ (d, 1H, $J = 5.0$ Hz, $\beta$), 8.33 (d, 1H, $J = 5.0$ Hz, $\beta$), 8.10 (d, 1H, $J = 5.0$ Hz, $\beta$), 8.07 (d, 1H, $J = 5.0$ Hz, $\beta$), 8.04 (d, 1H, $J = 5.0$ Hz, $\beta$), 7.69–7.67 (m, 6H, Ar-$o$), 7.64 (t, 1H, $J = 1.9$ Hz, Ar-$p$), 7.63 (t, 1H, $J = 1.9$ Hz, Ar-$p$), 7.62 (t, 1H, $J = 1.9$ Hz, Ar-$p$), 7.13 (s, 1H, $\beta$), 7.05 (s, 1H, fused five-membered ring), 1.47 (s, 18H, tert-butyl), 1.45 (s, 18H, tert-butyl), 1.43 (s, 18H, tert-butyl), 0.35 (s, 9H, TMS) ppm; $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta = 158.29$, 154.73, 149.24, 149.19, 149.17, 148.35, 147.41 (overlap), 146.89, 145.10, 143.79, 143.52, 142.55, 140.11, 139.92, 139.76, 138.18, 135.17, 133.09, 130.93, 129.85, 129.54, 128.93, 128.33, 127.81, 127.26, 126.71, 126.37, 126.02, 121.27, 121.11 (overlap), 120.29, 115.53, 35.11, 35.08 (overlap), 31.80, 31.77 (overlap),...
-0.92 ppm; UV-vis (CH2Cl2): $\lambda_{\text{max}}$ ($\varepsilon \text{ M}^{-1} \text{cm}^{-1}$) = 380 (52000), 427 (61000), 583 nm (4600); MS (APCI, negative): $m/z = 1026.5488$. Calcd for C67H80N4S8NiSi: 1026.5511 [M]\(^{-}\).

3b: $^1$H NMR (600 MHz, CDCl3) $\delta$ = 8.37 (d, 1H, $J = 5.0$ Hz, $\beta$), 8.34 (d, 1H, $J = 5.0$ Hz, $\beta$), 8.12–8.09 (m, 2H, $\beta$), 8.05 (d, 1H, $J = 5.0$ Hz, $\beta$), 8.02 (d, 1H, $J = 5.0$ Hz, $\beta$), 7.69–7.67 (m, 6H, Ar-o), 7.64 (t, 1H, $J = 1.9$ Hz, Ar-p), 7.63–7.61 (m, 2H, Ar-p), 7.12 (s, 1H, $\beta$), 7.05 (d, 1H, $J = 5.0$ Hz, $\beta$), 6.89 ppm; 13C NMR (151 MHz, CDCl3): $\delta$ = 158.15, 155.49, 149.29, 149.25, 149.21, 148.94, 148.33, 147.40, 146.89, 145.18, 143.84, 143.84, 142.48, 139.97, 139.81, 138.15, 137.91, 133.07, 130.91, 129.90, 129.58, 129.03, 128.35, 127.64, 127.32, 126.40, 126.01, 121.30, 121.18, 121.13, 120.35, 115.53, 35.11 (overlap), 31.81, 31.78 (overlap), 26.99, 17.08, −5.63 ppm; UV-vis (CH2Cl2): $\lambda_{\text{max}}$ ($\varepsilon \text{ M}^{-1} \text{cm}^{-1}$) = 381 (54000), 427 (63000), 583 nm (4700); MS (APCI, negative): $m/z = 1068.5956$. Calcd for C70H86N4S8NiSi: 1068.5981 [M]\(^{-}\).

3c: $^1$H NMR (600 MHz, CDCl3) $\delta$ = 8.38 (d, 1H, $J = 5.0$ Hz, $\beta$), 8.34 (d, 1H, $J = 5.0$ Hz, $\beta$), 8.12–8.09 (m, 2H, $\beta$), 8.09 (d, 1H, $J = 5.0$ Hz, $\beta$), 8.06 (d, 1H, $J = 5.0$ Hz, $\beta$), 8.01 (d, 1H, $J = 5.0$ Hz, $\beta$), 7.69–7.66 (m, 6H, Ar-o), 7.65 (t, 1H, $J = 1.9$ Hz, Ar-p), 7.64–7.61 (m, 2H, Ar-p), 7.10 (s, 1H, $\beta$), 7.08 (s, 1H, fused five-membered ring), 1.46 (s, 18H, tert-butyl), 1.45 (s, 18H, tert-butyl), 1.42 (s, 18H, tert-butyl), 1.10 (s, 9H, TBS), 0.29 (s, 6H, TBS) ppm; 13C NMR (151 MHz, CDCl3): $\delta$ = 158.20, 155.99, 149.69, 149.24, 149.20, 148.70, 148.43, 147.40, 146.89, 145.18, 143.84, 143.55, 142.48, 139.97, 139.81, 138.15, 137.91, 133.07, 130.91, 129.90, 129.58, 129.03, 128.35, 127.64, 127.32, 126.40, 126.01, 121.30, 121.18, 121.13, 120.35, 115.53, 35.11 (overlap), 31.81, 31.78 (overlap), 26.99, 17.08, −5.63 ppm; UV-vis (CH2Cl2): $\lambda_{\text{max}}$ ($\varepsilon \text{ M}^{-1} \text{cm}^{-1}$) = 381 (57000), 427 (63000), 584 nm (4900); MS (APCI, negative): $m/z = 1110.6405$. Calcd for C73H92N4S8NiSi: 1110.6450 [M]\(^{-}\).

Protodesilylation of 8α-Trimethylsilyl-7,8-dehydropurpurin 3a: 8α-Trimethylsilyl-7,8-dehydropurpurin 3a (17.8 mg, 16.5 mg) was placed in a reaction flask, and dissolved in THF (18 mL) and H2O (2.0 mL). After the addition of conc. HCl aqueous solution (12 M, 2.0 mL), the mixture was stirred at room temperature for 20 min. Then, the reaction was quenched by the addition of a saturated aqueous NaHCO3 aqueous solution, and the product was extracted with CH2Cl2 (3×25 mL). The combined organic layer was washed with brine and dried over Na2SO4. After removal of the solvent in vacuo, the residue was purified by silica gel chromatography eluting with CH2Cl2/hexane. Recrystallization of the separated solids from CH2Cl2/MeOH gave 4 (7.4 mg, 7.1 mg, 45%) of high purity.

4: $^1$H NMR (600 MHz, CDCl3) $\delta$ = 8.33–8.28 (m, 2H, $\beta$), 8.09 (d, 1H, $J = 4.8$ Hz, $\beta$), 8.04–8.00 (m, 2H, $\beta$), 7.98 (d, 1H, $J = 4.8$ Hz, $\beta$), 7.67 (d, 2H, $J = 1.9$ Hz, Ar-o), 7.65 (d, 2H, $J = 1.9$ Hz, Ar-o), 7.65–7.62 (m, 3H, Ar-o+Ar-p), 7.63–7.60 (m, 2H, Ar-p), 7.08 (s, 1H, $\beta$), 6.80 (d, 1H, $J = 5.5$ Hz, fused five-membered ring), 5.96 (d, 1H, $J = 5.5$ Hz, fused five-membered ring), 1.44 (s, 36H, tert-butyl), 1.41
(s, 18H, tert-butyl) ppm; $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta =$ 156.48, 150.95, 149.27, 149.21, 149.11, 148.51, 147.09 (overlap), 144.99, 144.04, 143.63, 142.54, 139.87, 139.68, 139.35, 138.12, 137.64, 135.19, 133.19, 130.99, 129.96, 129.41, 128.31, 128.25, 127.78, 127.49, 126.55, 126.35, 126.18, 121.34, 121.28, 121.11, 120.04, 114.57, 35.07 (overlap), 31.79, 31.78, 31.76 ppm; UV-vis (CH$_2$Cl$_2$): $\lambda_{\text{max}} (\varepsilon [\text{M}^{-1}\text{cm}^{-1}]) = 379 (57000), 425 (63000), 581$ nm (4700); MS (APCI, negative): $m/z = 954.5075$. Calcd for C$_{64}$H$_{72}$N$_4$Ni: 954.5116 [M$^-$.]

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